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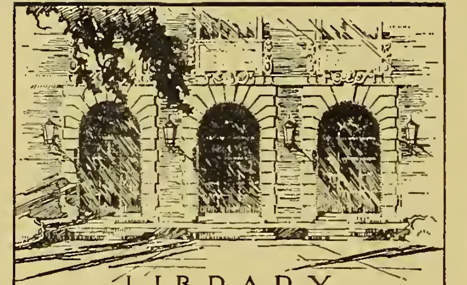

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ZINC ADSORPTION BY PRECIPITATED IRON ON LAKE BOTTOMS

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ACKNOWLEDGEMENTS

This report is submitted as a thesis in partial fulfillment of the requirements for the degree of Master of Science in Sanitary Engineering under the direction of Dr. John T. O'Connor, Associate Professor of Sanitary Engineering, University of Illinois.

The author wishes to express his most sincere appreciation to all those who advised and assisted him during the completion of this work. He wishes to especially thank Dr. John T. O'Connor for his guidance and enthusiastic support during the progress of the research.

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ABSTRACT

The objective of this research was to study the cycling of zinc in an artifical lake bottom. The cycling of zinc is related to the amount of adsorbent, precipitated iron floc and sediment, present on the lake bottom. By lowering the oxidation potential of the system, reducing conditions will cause the precipitated ferric hydroxide floc to go into solution, i.e. the iron is reduced from Fe^{+++} to Fe^{++}. With less adsorbent, more zinc should be in solution. The stability-field diagram is used as a tool for explaining the behavior of the system.

The research studies employed two artificial lake bottoms. One lake bottom had an Ottawa silica sand sediment, and the other, a control, had no sediment. The adsorption of zinc was also studied at pH 5 and 7. The data from these were used as guides in determining the relative quantities of zinc and iron to be used in the artificial lake bottoms and as guides in interpreting the behavior of the artificial lake bottoms. The oxidation potential of the lake bottoms were lowered with anaerobic bacteria; a preliminary study of biological adsorption was also made.

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I. Introduction

In natural lakes and reservoirs, the zinc concentration in the water has been reported to vary seasonally although the input of zinc to the lake remains constant.[1] The magnitude and mechanism involved in this seasonal variation or cycling are not fully understood. This report proposes to investigate the postulate that the seasonal cycling of zinc is related to the cycling of iron in a lake.

Since zinc always remains as a divalent cation, (Zn^{++} only), the solubility of zinc would not be expected to be a function of the oxidation-reduction potential (ORP or redox). A change in zinc equilibrium with a change in oxidation-reduction potential may be caused by one of two mechanisms. First, anaerobic bacteria which lower the ORP also produce carbon dioxide which lowers the pH. The shift in zinc equilibrium may then be caused by a change in pH produced by anaerobic bacteria. Second, the solubility of iron, a divalent cation, is dependent on the oxidation-reduction potential. A change in ORP could change the amount of precipitated ferric oxides in the lake bottom. Since ferric oxides can adsorb heavy metals, the return of precipitated iron will decrease the adsorptive capacity of the sediment on the lake bottom. Another possible cause for a decrease in adsorptive capacity is the destruction of organic adsorbents by anaerobic decomposition.[1] With a decrease in adsorptive capacity due to either a decrease in the quantity of organic adsorbents or of precipitated iron oxides, the sediment would be expected to release zinc and other adsorbed cations to the aqueous phase.

This report includes a discussion of the nature and permissible concentrations of zinc in natural waters, the nature, concentration, and

effect of reducing conditions on iron in natural waters, zinc adsorption by iron floc, and the utility of the stability-field diagram for predicting the cycling of zinc.

Laboratory experiments were conducted in an attempt to observe the cycling of zinc with respect to a decrease in the adsorptive capacity of precipitated iron floc returning to solution. Other experiments such as the effect of pH on zinc adsorption by iron floc, effect of age on zinc adsorption by iron floc, and adsorption of zinc by biological growths were performed only as control groups in the study of the cycling of zinc and not as separate experiments in themselves.

II. Survey of Literature

A. Nature of Zinc and Zinc in Natural Waters

Zinc is an important trace element for biological growth. Many enzymes and hormones contain zinc; for instance, the enzyme carbonic anhydrase is .33% zinc by weight.[18] Growth retardation in animals can be the result of zinc deficiency. In adult humans, the total zinc content of the body is about 2 grams. Daily zinc intake for adults is 10 - 15 mg. Zinc concentrations as high as 25 mg/l in drinking water have not affected the consumer's health. In general, stable zinc has no harmful effects on humans until concentration around 300 mg/l are encountered; nausea and gastrointestinal upsets occur at these high concentrations. The U. S. Public Health Service recommends a limit of 5 mg/l for zinc to prevent the undesirable aesthetic effect of taste.[24] Other animals, young fish in particular, are affected by lower concentrations of zinc. The incipient lethal level for Atlantic salmon is .42 mg/l in very soft water at 17°C.[20]

Although the harmful concentrations of stable zinc are small when compared with concentrations of other metal cations in water, such as sodium or calcium, the potentially hazardous concentrations for radioactive zinc are minute. In humans, zinc tends to concentrate in the prostrate gland, liver, and bones. The maximum permissible concentration of radioactive zinc in water for occupational exposure recommended by the International Commission on Radiological Protection is as follows:[7]

Nuclide	MPC	Time	Critical Organ
Zn^{65}	10^{-3} μc/cm^3	168 hr. week	Total Body
Zn^{69m}	7×10^{-4} μc/cm^3	168 hr. week	Lower Large Intestine
Zn^{69}	.02 μc/cm^3	168 hr. week	Stomach

For zinc-65 with a specific activity of 1.24×10^{-4} gm/curie,[10] the concentration of 10^{-3} μc/cm^3 of zinc-65 is equivalent to 1.24×10^{-7} mg/l. This concentration of zinc is extremely small when compared to the daily adult human intake of 10 - 15 mg/l. The importance of a sudden release of adsorbed radioactive zinc from the lake bottom sediments can readily be seen.

The zinc content of some natural lakes and reservoirs approaches 1 mg/l, e.g. Bear Lake, Idaho, contains .65 mg/l and Lake Michigan contains from .2 to .3 mg/l of zinc. A mean zinc content for most lakes and rivers appears to be on the order of .01 mg/l.[13] The solubility of zinc in distilled water is a function of pH and alkalinity. The solubility of zinc calculated from the solubility products

$$[Zn^{++}][OH^-]^2 = 4.5 \times 10^{-17}$$

$$[ZnO_2^{=}][H^+]^2 = 1.0 \times 10^{-29}$$

is about 5 mg/l at pH 7 and 250 mg/l of alkalinity.[12] The difference between the actual zinc content of natural waters and the theoretical solubility can be attributed, in part, to uptake of zinc by sediment. O'Connor and Renn have reported that zinc rapidly disappears, about 5 minutes, from an undersaturated zinc solution when suspended solids are present.[17] The uptake of zinc in natural waters is dependent upon the amount and kind of suspended material, the concentration of zinc in solution and the concentration of other ions.[1] Reducing conditions and pH also affect the equilibrium between zinc and suspended solids. In general, zinc adsorption

increases with increasing pH.[17,1] Zinc concentrations have been observed to increase with depth in stratified lakes.[1] This was taken as an indication that reducing conditions increase the zinc concentration in natural waters. Another indication of the effect of reducing conditions on the zinc equilibrium is that oxidized sediments take up five times as much zinc as reduced sediments.[1] O'Connor, Renn and Wintner also report that reducing conditions favor a higher concentration of zinc in solution.[19]

B. Nature of Iron and Iron in Natural Waters

Iron may exist in water as a trivalent or divalent cation; ferric ($Fe\underline{III}^{+}$), the oxidized form, and ferrous ($Fe\underline{II}$), the reduced form. The species of iron that predominates is dependent on both the pH and oxidation-reduction potential of the system and is best explained by a field-stability diagram. In general, at low pH and low ORP, the more soluble ferrous form of iron predominates, and at high pH and high ORP, the equilibrium favors the insoluble ferric form.

Iron floc is formed from hydrated ferric ions as follows:

$$[Fe(H_2O)_6]^{+++} + H_2O \rightleftharpoons [Fe(H_2O)_5OH]^{++} + H_3O^{+}$$
$$2[Fe(H_2O)_5(OH)]^{++} \rightleftharpoons [Fe_2(H_2O)_8(OH)_2]^{+4} + 2H_2O$$

This last tetrapostive-dimeric species is the first species of a series of polymers which form iron floc. As the charge on ferric iron decreases through coordination with hydroxo groups, repulsion between ions decreases and polymerization increases. Eventually, colloidal polymers and, finally, insoluble hydrous ferric oxide precipitates are formed.[23] The nature of the precipitated floc that forms is a function of pH conditions, the degree of polymerization, and the activity of other ions present. The physical structure of the floc may be block shape, rod-like,

or filamentous.[3] Besides polymerizing with itself, iron forms inorganic complexes with fluoride, sulfate, phosphate, carbonate, and many organic compounds. If iron is oxidized by exposure to air, less than .01 mg/l of Fe^{+++}, $FeOH^{++}$, and $Fe(OH)_2^+$ remain in solution and essentially all of the suspended iron can be removed by a .45 micron membrane filter.

Morgan and Stumm consider hydrous metal oxides as hydrated solid electrolytes containing a lattice structure having cation exchange characteristics resembling clay materials. With this view, the increase in exchange capacity with increase in pH is explained as an ion exchange process.[14] Others[11] make a distinction between removal of cations from solution by iron floc as coprecipitation and as physical adsorption. Still others make no distinction in the removal mechanism and use the term sorption. For the purposes of this paper adsorption will be a general term and not necessarily refer to physical adsorption.

Hutchinson reports that iron appears in natural waters in the range of .05 to .2 mg/l as ferric hydroxide, or as soluble or colloidal iron organic complexes. The vertical distribution of iron in lakes is similar to the vertical distribution of the redox potentials. The redox potential in turn is reflected by the oxygen curve. When oxidation-reduction potential is low in the hypolimnion, considerable amounts of ferrous iron will be released. If the redox potential continues to drop, hydrogen sulfide may form and the sulfide will precipitate the ferrous iron from solution.[6]

The exchange of dissolved substances between bottom sediments and water was studied by Mortimer.[15,16] While studying the exchange of dissolved substances between mud and water in lakes, Mortimer noted

that, during the winter, an "oxidized microzone" appeared on the surface of the bottom material. This oxidized zone was from 2 to 4 cm thick. At the water-mud interface, the redox potential was the same as the potential in the overlying water. At about 2 cm, E_7 (ORP at pH 7) was about +200 mv, and at 4 cm, the redox potential dropped to zero. At depths of about 4 cm or lower, the ferrous form of iron predominated, but no transfer of iron from the reduced zone to the water occured because of the oxidized microzone. During the summer months, from July through September, the lake stratified, the dissolved oxygen dropped, the redox potential dropped, and the oxidized microzone disappeared. With no oxidized zone, the ferrous iron went into solution. As much as 18 grams of iron were released per square meter; this corresponds approximately to 1.4 mg/l if the lake were fully mixed. Before the iron returned to solution, the E_7 dropped to about +180 mv.

C. Applicability of Stability-Field Diagram

Oxidation-reduction potential measurements have been applied to metal plating waste treatment, sewage treatment, bleach manufacturing, and has been used for classifying bacteria (aerobic +400 to -200 mv and anaerobic +50 to -400 mv).[9] This measurement is related to the free energy involved in the reaction concerned. The potential or electromotive force of the cell under reversible conditions measures the free energy of the cell reaction. This occurs when no current is flowing.[2] The actual measurement is made using platinum and calomel electrodes. Because of the limitations of the electrodes, the measured ORP is influenced by all oxidants and reductants present. Other interferences in ORP measurement are due to coated electrode surfaces, a memory effect on the platinum

electrode caused by exposure to strong oxidants or reductants, pH, and temperature (1 mv/°C).[8]

For the oxidation reduction potential to be most useful, the system must be reversible and a minimum concentration of reactants must be present.[21] In a reversible reaction, any change in current produced by an increase or decrease in electromotive force causes a shift in the equilibrium of the reactants. This shift is completely reversible. An example of this type of reaction is $Fe^{+3} + e \rightleftharpoons Fe^{+2}$. An irreversible reaction will consume current before a shift in equilibrium takes place.[21] Many of these irreversible reactions occur in natural waters. Some of these reactions involve iron complexes, the sulfur series, the nitrogen series, organic redox systems,[10] and oxygen. Oxygen is a dominating irreversible oxidation-reduction couple. When dissolved oxygen is present, even at low concentrations, the reversible ferrous-ferric couple may act as an electron-transfer catalyst.[22] In such a case, the measured ORP would be a mixed potential with oxygen dominating the measured potential.

In general, the oxidation-reduction potential measured under natural conditions will be a mixed potential because of the presence of dissolved oxygen, sulfates, nitrates, or organic material. Even though the potential measured is not indicative of any one component of the system nor does it reflect the true thermodynamic condition, the oxidation-reduction potential is a useful tool for predicting the species of iron that predominates in a given system. The field-stability diagram is a plot of potential (Eh), the electromotive force of the system with respect to a hydrogen electrode, versus pH (see Figure 1). The vertical lines are calculated from solubility products and other boundaries are calculated using the Nernst equation.[4]

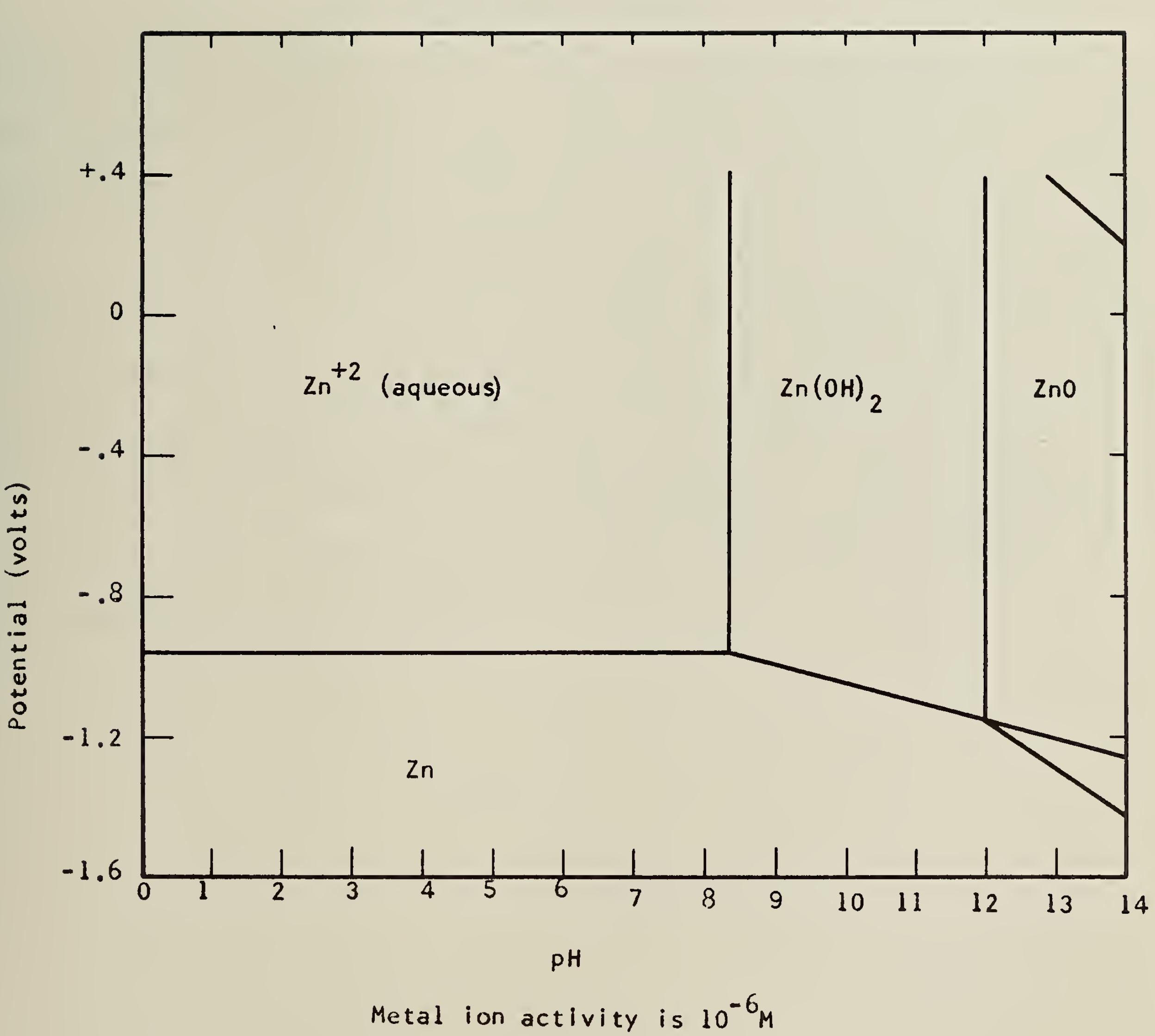


Figure 1

Stability-Field Diagram for Zinc
(After Pourbaix, C&EN, April 1965)

$$Eh = Eo + \frac{.0592}{n} \log \frac{(\text{activity of oxidants})}{(\text{activity of reductants})}$$

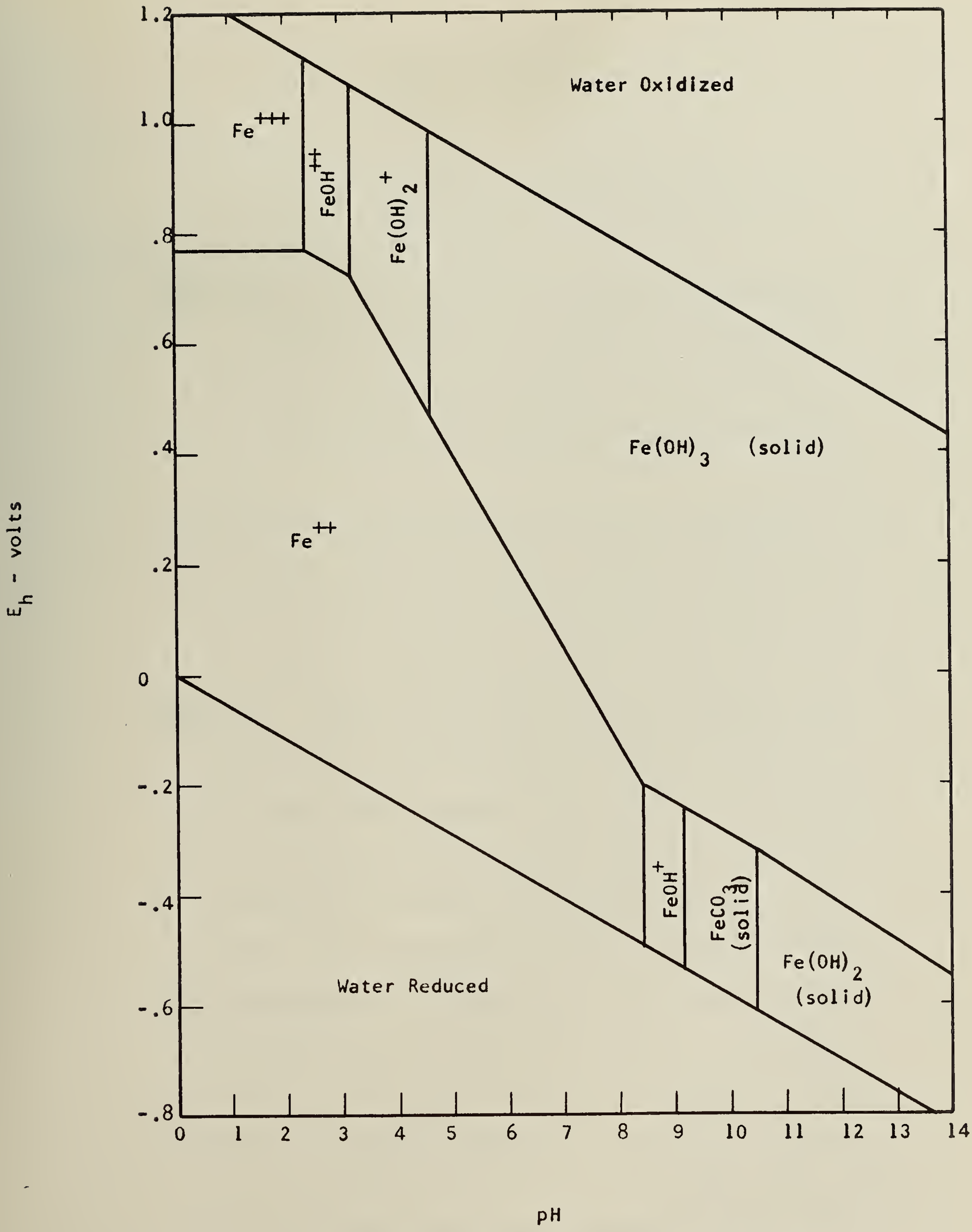
where Eh = potential with respect to hydrogen electrode

Eo = standard potential

n = number of moles of electrons involved.

Boundary lines are drawn for equal activities of each ionic species. The field-stability diagram does not predict absolute quantities of material present nor the rate at which equilibrium is attained.

The stability-field diagram for zinc is given in Figure 2. An earlier statement in this paper that implied that the solubility of zinc is independent of reducing conditions should be qualified, for ionic zinc can be reduced to the metal zinc under extreme reducing conditions. Within the boundaries of Eh and pH encountered in natural systems, is present in the Zn^{++} state only. As a result, only the pH influences zinc solubility in natural waters.



Total Activity of Iron is 10 mg/l and 100 mg/l of Bicarbonate

Figure 2

Stability Field Diagram for Iron

III. Laboratory Experiments - Procedure & Materials

A. General Procedure

In the laboratory experiments, the following general procedures were used unless otherwise noted.

Stable Zinc - A stock solution of stable zinc was prepared by dissolving .05 grams of zinc metal in concentrated hydrochloric acid and diluting to 500 mg. This solution has a strength of 1 mg of zinc per 10 mg of solution.

Iron Solution - A stock solution of iron was prepared by dissolving 1.78 grams of $FeCl_2 \cdot 4H_2O$ in hydrochloric acid and diluting to 500 ml. This solution has a strength of 10 mg of iron per 10 ml of solution.

Alkalinity - Alkalinity was added as sodium carbonate, but expressed as calcium carbonate. Whenever alkalinity was added, sodium carbonate was measured in the dry form and then added directly to the solution. In most of the experiments, the alkalinity is 200 mg/l as calcium carbonate; this corresponds to 212 mg/l of sodium carbonate.

Zinc Determination - The radioactive zinc-65 tracer was used throughout the experiments to facilitate the determination of zinc. A tracer solution was so prepared that the addition of 10 ml of tracer per liter of solution would raise the count rate of a 10 ml solution sample 2000 counts per minute above background. The amount of zinc in the tracer solution was computed as follows:

Stock tracer solution = 1 mc/50 ml

= .02 mc/ml

One ml stock tracer solution added to 50 ml of water to form tracer solution used in experiments.

$$\text{Tracer solution} = \frac{.02 \text{ mc}}{50 \text{ ml}} = .0004 \text{ mc/ml} = .4\ \mu\text{c/ml}$$

Specific activity of tracer at time of shipment =

$$476 \text{ mc/gm} = .47\text{C}\ \mu\text{c}/\mu\text{g}$$

Since the tracer was shipped in the fall of 1965, approximately 2 half-lives of zinc-65 tracer had elapsed. Therefore, using a specific activity of .119 μc/μg:

Zinc concentration in tracer solution =

$$\frac{.4\ \mu\text{c/ml}}{.119\ \mu\text{c}/\mu\text{g}} = 3.36\ \mu\text{g/ml}$$

In the experiments, the addition of 10 ml/l of the zinc tracer solution increased the zinc concentration by 3.36 μg/l = .0336 mg/l. This addition of zinc was small as compared to the total zinc concentration and was neglected.

Iron Determination - The general procedure for iron measurements is the same as that outlined in Standard Methods[25] with the exception that both sample and reagent quantities were reduced. All reagents were prepared according to Standard Methods. The procedure used for the iron determination was as follows:

1. 10 ml sample placed in 50 ml flask
2. 1 ml concentrated hydrochloric acid added to flask
3. 1 ml hydroxylamine solution added to flask

4. Glass beads added to flask and flask heated to boiling
5. Contents cooled to room temperature and transferred to a 25 ml volumetric flask
6. 5 ml ammonium acetate buffer
7. 2 ml phenanthroline solution
8. Dilute to mark, mix contents, and allow 10 - 15 minutes for maximum color development.

The color samples were then read on a Spectronic 20 at 510 mμ. A standard curve of log transmittance versus concentration was prepared.

pH Meaurements - A Photovolt Model 180 expanded scale pH meter was used for all pH measurements. Solutions of hydrochloric acid or sodium hydroxide were used for solution pH adjustment.

Oxidation-Reduction Potential - A Photovolt Model 180 pH meter was used for potential measurements. The instrument was equipped with an adaptor for a combination platinum-calomel probe.

Filtration of Samples - Whenever a separation between the solution and suspended material was made, a new membrane filter of .45 μ was used. Typically, 10 ml samples were filtered to obtain the zinc and iron concentrations in solution.

Zinc - Zinc was determined by Zn^{65} tracer techniques using a gamma scintillation counter. Samples were counted for 10 minutes.

Throughout the experiments, care was taken to prevent contamination of the samples. Demineralized water was used to prepare all solutions, chemicals were reagent grade, and all glassware was washed with a hydrochloric acid solution, rinsed with tap water, then distilled water, and finally demineralized water.

B. Effect of pH on Zinc Adsorption by Iron Floc

As a control measure, the effect of pH on the adsorption of zinc by glassware and by iron floc was investigated. The adsorption of zinc by glassware was observed by adding 1 mg/l of zinc and 200 mg/l of alkalinity to one liter of water in a glass beaker. The pH of the solution was 3.4 after only the zinc was added, and the count rate at this pH was taken to be equivalent to 1 mg/l of zinc. The alkalinity was then added and the pH was raised with sodium hydroxide. The effect of pH on zinc adsorption by iron floc was investigated by using a solution of 1 mg/l of zinc, 50 mg/l of iron, and 250 mg/l of alkalinity.

C. Adsorption of Zinc by Iron Floc

Again, as a control measure, the adsorption of zinc by iron floc was studied at pH 5 and pH 7. In these experiments, a two liter solution containing 1 mg/l of zinc and 200 mg/l of alkalinity was mixed with compressed air at pH 7 and with air and CO_2 at pH 5. Iron was then added in known quantities to this solution, and then the zinc concentration of the solution filtrate was obtained after 10 to 15 minutes of mixing. The initial zinc concentration was determined at a low pH before either alkalinity or iron was added. The pH was adjusted with sodium hydroxide or hydrochloric acid.

D. Artificial Lake Bottoms

The artificial lake bottoms were an attempt to simulate the hypolimnion of a stratified lake. Large glass jars were used to create the artificial lake bottoms. Each jar was twelve inches deep and six inches in diameter and contained four liters of solutions.

Dissolved oxygen contents similar to those encountered in natural hypolimnions during late summer were produced by stripping the water of oxygen with compressed nitrogen and by maintaining an atmosphere of pure nitrogen above the water surface. A plastic cover containing sampling holes was sealed to the top of the jar with tape. The complete removal of oxygen and the lowering of the oxidation-reduction potential was accomplished employing bacteria. After the water was stripped of oxygen, seed organisms obtained from anaerobic digester and yeast extract were added to the jar. Provisions for adding bubbling carbon dioxide through the jar were also provided.

Two jars were used in each experiment. One jar contained a sand sediment and the other jar had no sediment; all other initial conditions and additions of yeast, carbon dioxide, or oxygen were the same for both jars. The bottom sediment was 750 grams of acid-washed Ottawa silica sand that passed a #20 sieve but was retained on a #25 sieve. Throughout the experiment, the contents of these jars were not changed. In studies conducted at pH 7, the pH of each jar was readjusted to pH 7 immediately before sampling. After 14 days at pH 7, the pH of both jars were lowered using compressed carbon dioxide. At this lower pH, no pH adjustment prior to sampling was necessary.

The jars initially contained 1 mg/l of zinc, 10 mg/l of iron, and 200 mg/l of alkalinity. Yeast extract was added periodically to lower the oxidation-reduction potential by stimulating bacterial growth. Sampling consisted of recording the pH (or adjusting if necessary), recording ORP, obtaining and filtering samples, obtaining zinc counts, and finally determinding the iron content of filtered samples.

Figure 3 is a diagram of a typical jar used during this experiment.

E. Effect of Age on Zinc Adsorption by Iron Floc

The effect of age on the adsorption capacity of iron floc was studied as a control for the artificial lake bottoms. Two experiments were run -- one at pH 7 for six days and the other at pH 5 for 9 days. In these experiments, the initial volume was two liters, zinc concentration was 1 mg/l, iron was 5 mg/l, alkalinity was 200 mg/l, and mixing was accomplished by compressed air.

F. Adsorption of Zinc by Biological Growth

Again, as a control, the adsorption of zinc by the bacteria used for producing reducing conditions was investigated. A jar similar to those used for the artificial lake bottoms, had been used to acclimate the anaerobic bacteria to the yeast extract. This jar had received yeast extract for about a month before the experiment started. A known quantity of zinc was then added to this jar, and the amount of zinc remaining in solution was then recorded over a period of days. The amount of bacteria in this jar is not related to the amount of bacteria in the artificial lakes, but was of the same order of magnitude.

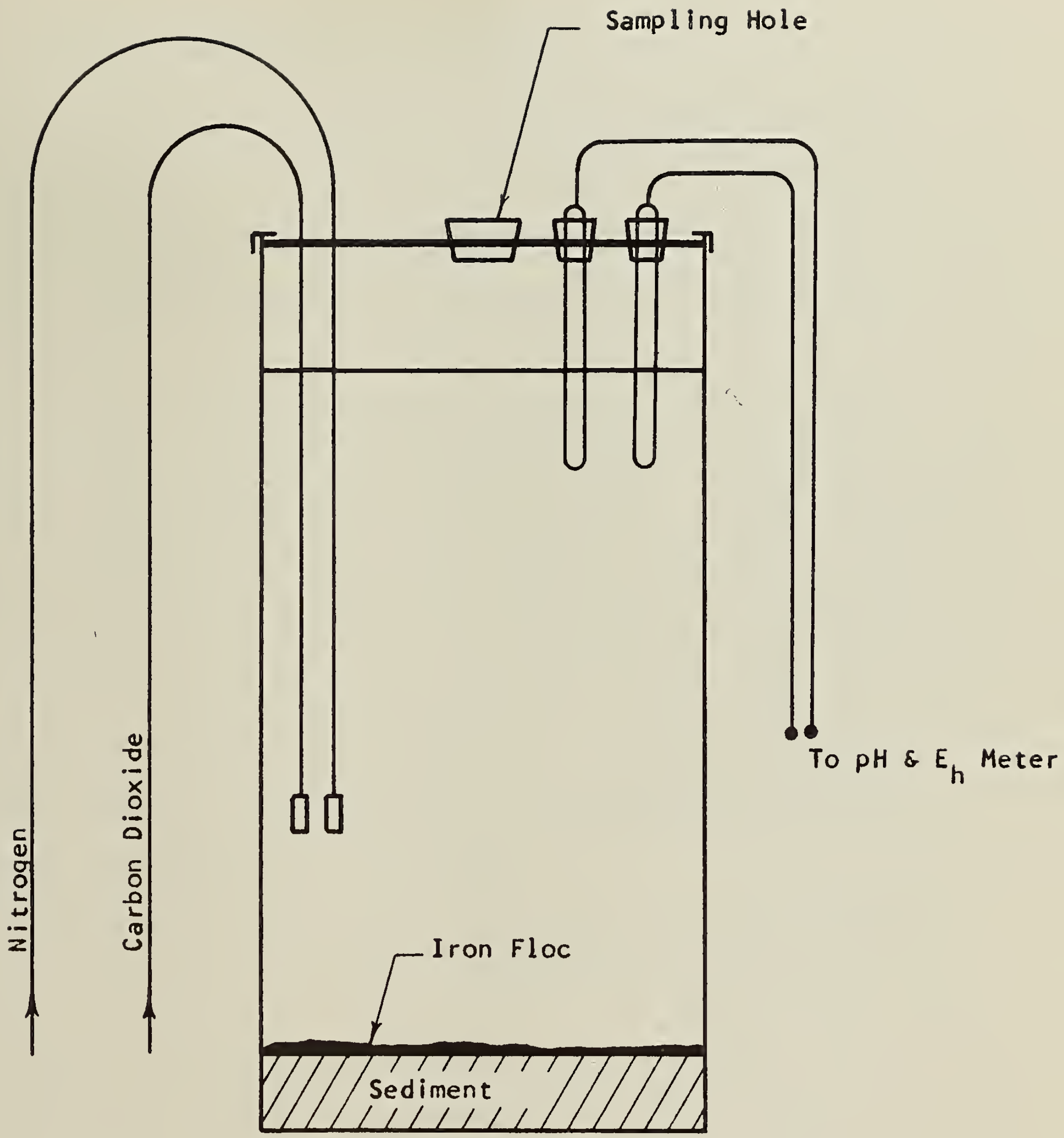

Sampling Hole
To pH & E_h Meter
Nitrogen
Carbon Dioxide
Iron Floc
Sediment

Figure 3
Diagram of Apparatus

IV. Results and Discussion

A. Effects of pH on Zinc Adsorption by Iron Floc

Without knowledge of the adsorption capacity characteristics of the glass container, the adsorption capacity reported for sediemnts or iron floc could be misleading. The adsorption characteristics for the glass breaker containing 200 mg/l of alklainity and 1 mg/l of zinc are given in Table 1.

When pH 8.23, is exceeded, the decrease of zinc in solution is attributable to the precipitation of zinc as $Zn(OH)_2$. From theoretical consideration of solubility products, zinc is soluble in excess of 1 mg/l when the pH is less than 7.5 and alkalinity is 250 mg/l.[19] For the data given, zinc is lost from solution even in the pH range 5.40 to 7.14. This may be attributed to adsorption by the glassware. In general, as long as the pH is lower than 7.5, zinc adsorption by the glassware might be expected to be on the order of 10 - 15 per cent.

The effect of pH on the adsorption capacity of bottom sediments has been reported to be very significant by many investigators. Similarly, a change in pH would be expected to affect the adsorptive capacity of iron floc. The results obtained from a solution containing 1 mg/l of zinc, 50 mg/l of iron, and 250 mg/l of alkalinity is given in Table 2. This data demonstrates the dependence of the adsorption capacity of iron floc on pH. Control of pH is very important in the study of zinc adsorption by iron floc.

Table 1

Zinc in Solution Versus pH

pH	Zinc in Solution - mg/l
3.40	1
5.40	.97
6.02	.90
6.66	.77
7.14	.81
7.61	.70
8.23	.86
8.55	.45
9.10	.31

Table 2

Effect of pH on the Adsorptive Capacity of Iron Floc

pH	Zinc in Solution - mg/l
5.4	.88
5.7	.79
6.0	.62
6.1	.65
6.4	.45
6.8	.22

B. Adsorption of Zinc by Iron Floc

In the artificial lake bottoms, precipitated iron will be released to the solution. When this happens the amount of precipitated iron and hence the adsorptive capacity of the bottom material will be decreased and zinc will return to solution. Before any measureable amount of zinc will be released to solution, the adsorptive capacity of the sediment or iron floc must be less than that required to adsorb most of the zinc. To determine this relationship, the adsorptive capacity of iron floc was determined at pH 7 and pH 5. In both experiments, the initial zinc was 1 mg/l and alkalinity was 200 mg/l. The results are given in Table 3 for pH 7 and in Table 4 for pH 5.

From the data in Table 3, it appears that nearly all the iron must go into solution before appreciable amounts of zinc are released in solution. From Table 4, more than three mg/l of iron must be precipitated before a significant amount (20 per cent) of zinc is adsorbed. These observations were useful aids in interpreting the results from the artificial lake bottoms.

C. Artificial Lake Bottoms

The first attempt (pH 7) to observe the cycling of zinc by varying the amount of iron precipitate did not show any significant cycling as shown in Figures 4 and 5. In the artificial lake bottom that had no sediment (pH 7), the iron slowly began to return to solution, but the amount of iron that remained precipitated (6.5 mg/l) had more than enough adsorptive capacity to prevent the zinc from returning to solution. The same is also true for the jar containing the sediment.

Table 3

Adsorption Capacity of Iron Floc for Zinc at pH 7

Iron (mg/l)	Zinc in Solution (mg/l)
0	1
2.5	.312
5	.192
7.5	.11
10	.05

Table 4

Adsorption Capacity of Iron Floc for Zinc at pH 5

Iron (mg/l)	Zinc in Solution (mg/l)
0	1
1	.815
1.5	.819
2	.910
2.5	.870
3	.855
4	.795
5	.758
6	.686
10	.630
15	.577

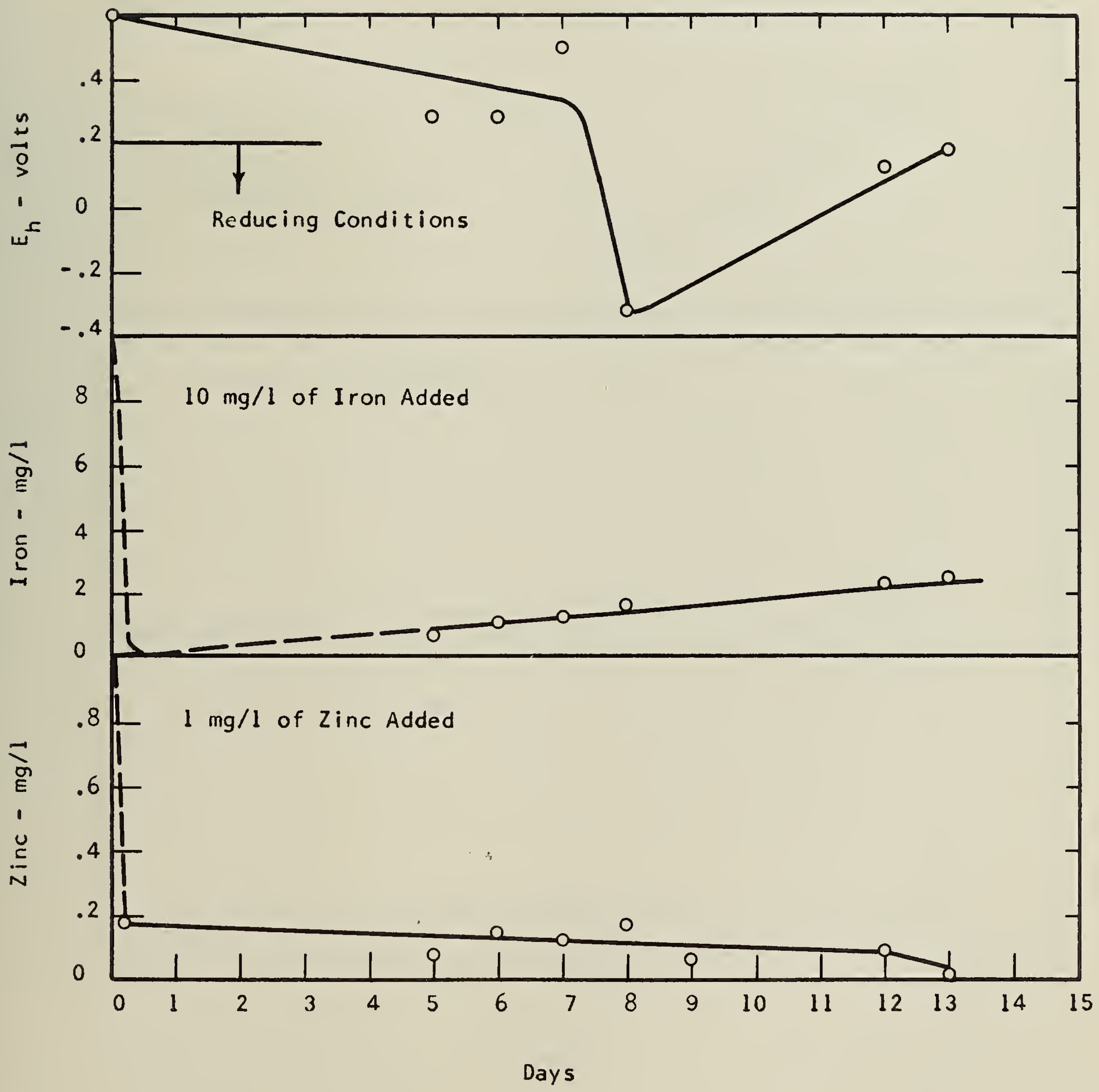


Figure 4

Artificial Lake Bottom - No Sediment - pH 7

Iron and Zinc in Solution

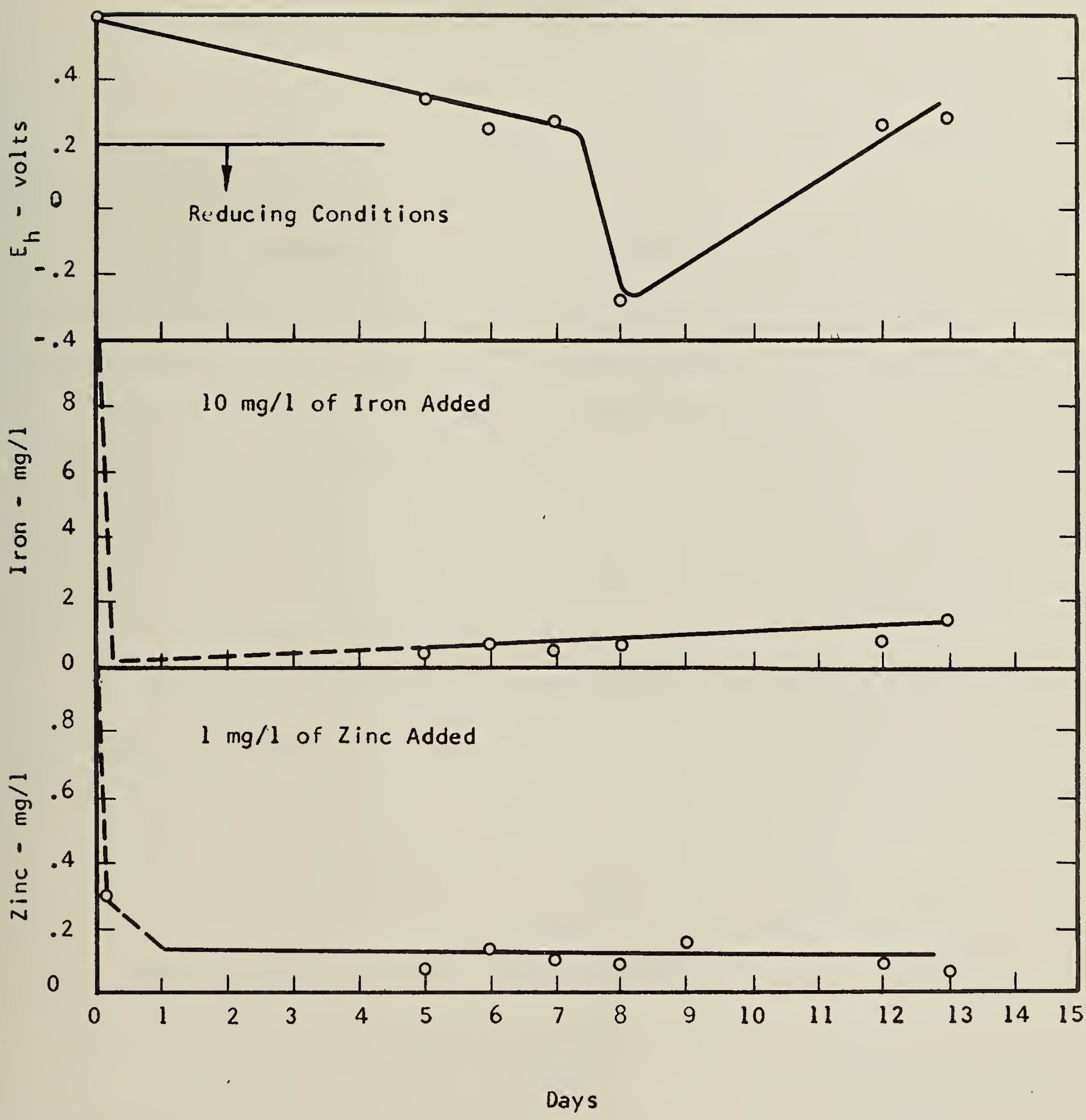


Figure 5

Artificial Lake Bottom - Sediment - pH 7

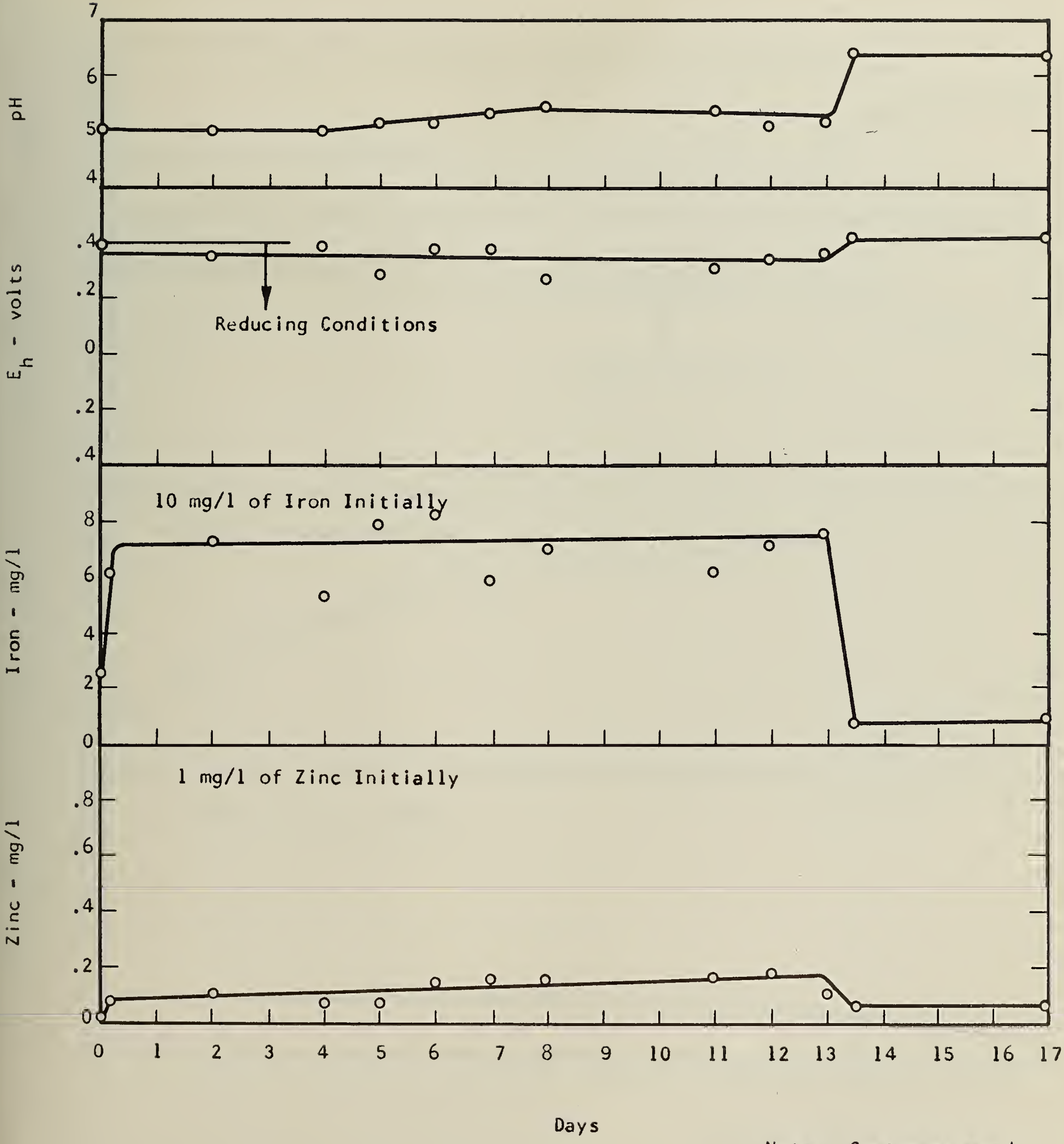
Iron and Zinc in Solution

From Figure 2, it appears that the Eh of the system must be below +200 mv before iron begins to return to solution. In both jars at pH 7, the Eh remained below +200 mv for five days. The iron in the jar with no sediment was returning slowly to solution; while in the jar with sediment, no return of iron was noted.

A possible cause for no zinc return and for little or no iron return could stem from the unstable pH conditions. Before each run, the pH was adjusted to 7.00 ± .05. The pH was always initially above 7. In the jar containing sediment, the initial pH increased to 8.3 on one day, and in the jar without sediment the pH climbed to 7.5. The drift in pH was believed to be due to stripping with nitrogen. Precipitation of zinc may have occurred at high pH as well as the precipitation of iron carbonates and oxides.

To stabilize the pH and to avoid possible precipitation of zinc, the pH of these two jars were then lowered with compressed carbon dioxide. The results of this change is shown on Figures 6 and 7. In both cases, considerable amounts of iron went into solution. The return of iron to solution in the artificial bottom containing sediment shows a good relationship between iron in solution and Eh. The Eh for return of iron to solution appeared to be about +400 mv at pH 5.

In both cases at pH 5, three mg/l or less of precipitated iron remained in the system. From Table 4, about .8 mg/l of the zinc should be in solution. The reason for more zinc not returning to solution is attributed to zinc adsorption onto the biological growth.

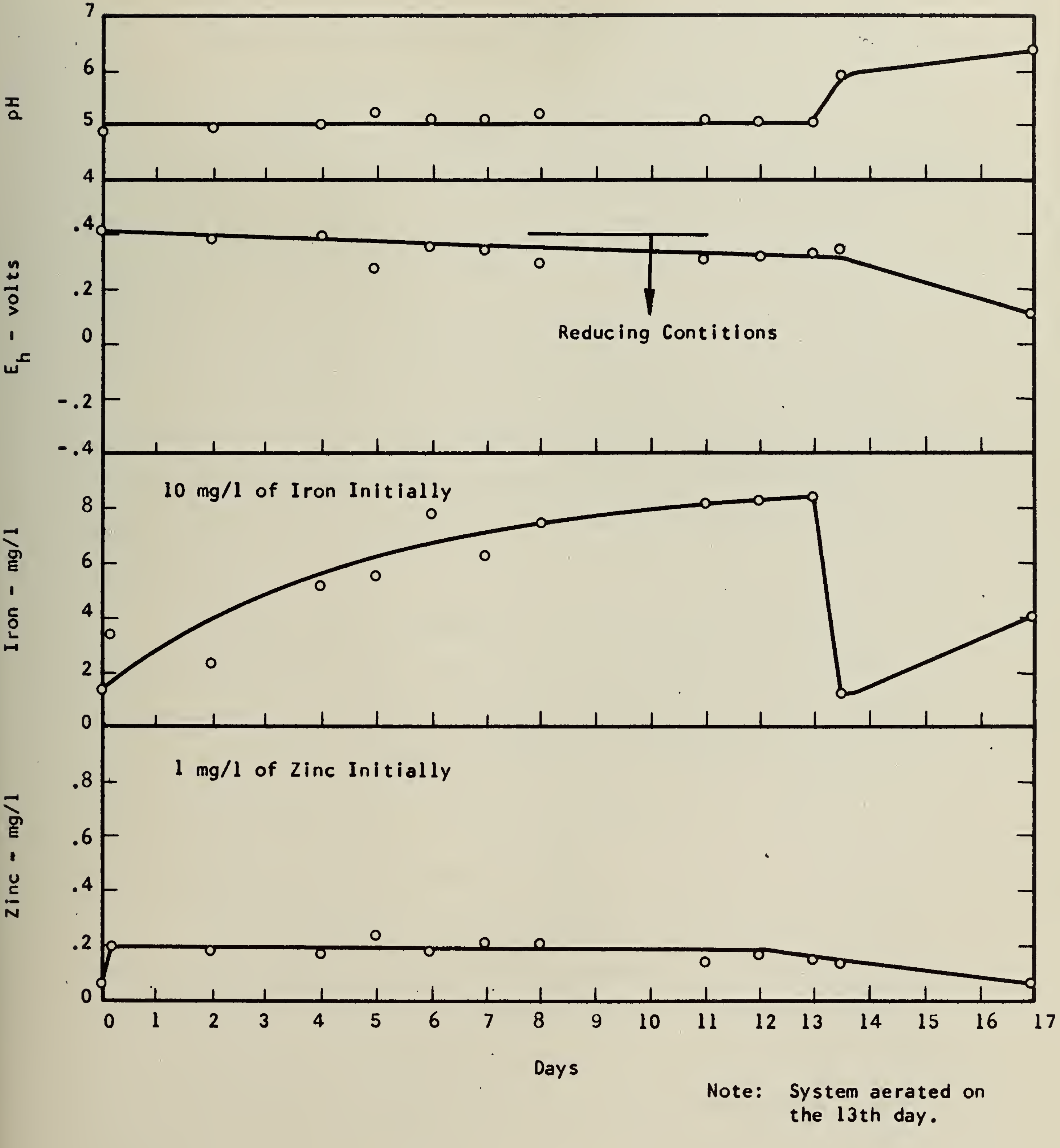


Note: System aerated on the 13th day.

Figure 6

Artificial Lake Bottom - No Sediment - pH 5

Iron and Zinc in Solution



Note: System aerated on the 13th day.

Figure 7

Artificial Lake Bottom - Sediment - pH 5

Iron and Zinc in Solution

After thirteen days, the system was aerated. The pH of both systems rose to around 6.0, the iron in solution decreased, and the zinc in solution decreased. This decrease in zinc can be attributed to adsorption onto the 7 or 8 mg/l of newly formed iron precipitate or to increased adsorption at the higher pH. From Table 4, 8 mg/l of iron floc are capable of adsorbing .7 mg/l of zinc.

D. Effect of Age on Zinc Adsorption by Iron Floc

As another control to aid in the understanding of the adsorption of zinc by iron floc, the change in adsorptive capacity of floc with time was studied at pH 5 and 7. The data obtained from experiments using 1 mg/l of zinc, 5 mg/l of iron, and 200 mg/l of alkalinity as in Tables 5 and 6.

In both cases of aging the iron floc, little differences of zinc in solution resulted. At pH 7, the zinc concentration remained at about .18 mg/l, and at pH 7, the zinc remained near .8 mg/l. In general, no significant increase or decrease in the adsorption capacity of zinc was noted for the period of time studied.

E. Adsorption of Zinc by Biological Growth

Since the amount of zinc in solution in the artificial lake bottoms at pH 5 was less than expected, the possibility of adsorption by the bacteria was considered. Although the amount of biological growth in this experiment is not the same as the growth in the artificial lakes, the significance of the amount of zinc adsorbed by the bacteria is shown in Table 7.

Table 5

Change in Adsorption Capacity of Iron Floc
With Time at pH 7

Time	Zinc in Solution
¼ hr.	.10
½ hr.	.12
3/4 hr.	.21
1 hr.	.16
2 hr.	.24
5 hr.	.15
1 day	.16
2 days	.17
6 days	.20

Table 6

Change in Adsorption Capacity of Iron Floc
With Time at pH 5

Time	Zinc in Solution
1 days	.73
3 days	.84
4 days	.85
5 days	.77
9 days	.87

Table 7

Zinc Uptake by Biological Growth

Time (days)	Zinc in Solution (mg/l)	pH
0	.67	5.90
1	.65	5.72
5	.54	5.60
6	.44	5.48
7	.55	5.52
11	.31	5.55

The initial zinc concentration was 1 mg/l. The mass of suspended solid in this system was 130 mg/l of solids dried for 24 hours in a desiccator. Although the quantity of yeast extract added to this jar is unknown, the total amount of yeast extract added to this system was less than the amount added to the artificial lake bottoms.

V. Conclusions

1. Precipitated iron can adsorb significant amounts of zinc.
2. The adsorptive capacity of precipitated iron for zinc is greatly influenced by pH.
3. The adsorptive capacity of iron floc for zinc does not change markedly when the floc is aged two weeks.
4. Biological growth can adsorb a significant amount of zinc.
5. The stability-field diagram is a useful tool in predicting the predominate species of iron. In this manner, changes in the adsorptive capacity of bottom sediments can be predicted.
6. The cycling of zinc produced by a decrease in adsorptive capacity of bottom sediments brought about by a return of precipitated iron to solution although not clearly demonstrate in this experiment, nonetheless, may be a possibility.

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VII. Appendix A

A. Calculations For Oxidation-Reduction Potential Measurements

$$Eh = Eo + E + \text{correction}$$

where

Eh = potential with respect to a hydrogen electrode

Eo = voltage of reference electrode

E = voltage observed with the platinum and calomel electrodes

The potential for a standard saturated calomel electrode is usually taken as 246 mv at 25°C. Therefore Eo = 246 mv.

Determination of the correction factor is a bit more involved. To obtain a stable, reproducible potential for calibrating the ORP measurement, a quinhydrone solution is used. Because the solution is an equimolar mixture of quinone and hydroquinone, the Nernst equation reduces to:

$$E_{(volts)} = .6994 - .000198\ (T)\ \ pH$$

where T is in degrees Kelvin.

If quinhydrone is added to a pH 4 buffer solution and if the temperature is 25°C, the oxidation-reduction potential of the system should be:

$$Eh = .6994 - (.000198)(298)(4) = .464 \text{ volts}$$

The reading on ORP meter should then be as follows:

$$\begin{aligned} E &= Eh - Eo \\ &= 464 - 246 \\ &= 218 \text{ mv} \end{aligned}$$

If the meter does not read 218 mv, a correction must be applied at all future ORP measurements. This correction should be calculated each time ORP measurements are made.

Example

ORP reading during standardization = 250 mv

Reading should have been 218 mv

Therefore correction = -32 mv

Now

$Eh = E + (246 - 32) = E + 214$

Appendix B

Data For Artificial Lake Bottoms at pH 7

No Sediment

Day	Eh(mv)	Iron in Solution (mg/l)	Zinc in Solution (mg/l)
0	517		.18
5	282	.35	.09
6	286	.55	.15
7	460	.60	.13
8	-308	.75	.18
9			.07
12	126	2.3	.07
13	188	2.4	.01

With Sediment

Day	Eh(mv)	Iron in Solution (mg/l)	Zinc in Solution (mg/l)
0	535		.30
5	332	.30	.08
6	236	.70	.14
7	268	.50	.10
8	-288	.75	.09
9			.15
12	256	.70	.09
13	273	1.3	.05

Yeast extract added on days zero and seven after the data was taken for the day.

Appendix C

Data for Artificial Lake Bottoms at pH 5

No Sediment

Day	pH	Eh(mv)	Iron in Solution (mg/l)	Zinc in Solution (mg/l)
0	5.00	387	6.3	.04
2	5.03	347	7.4	.11
4	5.03	394	5.2	.07
5	5.12	282	7.8	.06
6	5.08	372	8.2	.15
7	5.28	370	5.9	.16
8	5.40	272	7.0	.16
11	5.31	296	6.1	.16
12	5.04	331	7.0	.19
13	5.07	352	7.5	.11
13½	6.32	407	.7	.035
17	6.26	406	.8	.031

With Sediment

Day	pH	Eh(mv)	Iron in Solution (mg/l)	Zinc in Solution (mg/l)
0	4.90	412	3.4	.20
2	4.96	372	2.2	.18
4	4.99	399	5.1	.17
5	5.24	272	5.7	.24
6	5.12	362	7.8	.18
7	5.12	330	6.1	.21
8	5.18	285	7.4	.21
11	5.13	311	8.1	.15
12	5.06	322	8.2	.17
13	5.09	337	8.3	.15
13½	5.85	367	1.3	.14
17	6.40	86	4.1	.052

Yeast extract added on days 4, 6, and 8 after data for the day was taken.

Aeration began on the thirteenth day.

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